

Determination of plutonium and americium in environmental samples by inductively coupled plasma sector field mass spectrometry and alpha spectrometry

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Abstract

Application of inductively coupled plasma sector field mass spectrometry (ICP-SFMS) for the determination of americium and plutonium in environmental samples is described in comparison with alpha spectrometry. A sequential sample preparation method was employed using a co-precipitation step for pre-concentration and a separation step applying extraction chromatographic resins. The average recovery of sample preparation calculated from the concentration of the tracer before and after sample treatment was better than 80%. The method development focused on the elimination of possible interferences in mass spectrometric analysis caused by molecular ions (e.g. $^{200}\text{Hg}^{40}\text{Ar}^+$, $^{204}\text{Pb}^{36}\text{Ar}^+$, $^{208}\text{Pb}^{16}\text{O}_2^+$ or $^{238}\text{U}^1\text{H}^+$) employing matrix separation and desolvation prior to ICP-SFMS analysis. The effect of N_2 gas on signal intensity and oxide ratio was investigated. A two-fold signal improvement was obtained by adding $5 \text{ ml min}^{-1} \text{ N}_2$ to the sample gas after the desolvation system. For ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{241}Am limit of detection (LOD) of 15, 9.2, 14 and 104 fg g^{-1} was achieved, respectively. Calculation of LOD was based on three times standard deviation of the method blank solution. Absolute detection limit was calculated to be 10–25 fg. For all investigated actinides the precision of the analysis was in the range 0.8–3% relative standard deviation. Results from the analysis of certified reference materials (IAEA-384 and IAEA-385) showed good agreement with recommended values and data available in the literature. The method was applied for analysis of environmental samples originated from Chernobyl and from Mayak region. The possibility of the determination of the origin and date of pollution was demonstrated using isotopic data obtained by ICP-SFMS and alpha spectrometry.

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1. Introduction

Anthropogenic radionuclides have been released into the environment from several sources, e.g. nuclear weapon tests, fuel reprocessing and nuclear power plant accidents (e.g. Chernobyl or Mayak). Plutonium and americium can cause health hazards even in small concentrations due to their extremely high radiotoxicity. Moreover, the long-term threat of these radionuclides (half-lives of ^{239}Pu , ^{240}Pu and ^{241}Am are 24 110, 6560 and 432 years, respectively) created an increasing need for environmental monitoring of these actinides.

Since radiochemical methods, such as alpha spectrometry, are relative simple and inexpensive techniques, they have been most frequently used for the determination of radionuclides (e.g. ^{238}Pu , $^{239+240}\text{Pu}$, ^{241}Am) in samples of environmental origin [1–3]. However, the ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ – which is characteristic for the origin of plutonium (i.e. weapon test or reactor origin) – could not be determined by alpha spectrometry, because of their similar alpha-energies (5.15 and 5.16 MeV). Another disadvantage of alpha spectrometry is the relatively long measurement time, especially for analysis of environmental samples with low actinide concentration.

Mass spectrometric techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), thermal ionisation mass spectrometry (TIMS), and accelerator mass spectrometry

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(AMS) are also applied to obtain precise isotopic information on radionuclides [4]. Although TIMS and AMS can provide low detection limits, and both techniques provide precise isotope ratio information, the relatively high analysis cost, time consuming sample preparation and the complicated operation compared to inductively coupled plasma mass spectrometry prevented their routine application for the analysis of radionuclides in the environment. Therefore inductively coupled plasma mass spectrometers (ICP-MS) – especially the double-focusing magnetic sector instruments (ICP-SFMS) – have become a powerful alternative technique for the determination of radionuclides in environmental samples [5–7]. The ICP-SFMS technique combines the possibilities of high sensitivity multielemental and isotopic analysis with rapid analysis capabilities. Moreover, ICP-SFMS can be coupled on-line to high performance liquid chromatography (HPLC) or capillary electrophoresis (CE), which combinations decrease efficiently the analysis time and increase sample throughput [8,9]. Although, the ICP-SFMS technique provides considerably shorter analysis time than alpha spectrometry, the determination of some radionuclides, e.g. ^{238}Pu is limited by isobaric interferences [10]. Therefore, alpha spectrometry and ICP-SFMS can be used as complementary techniques for the analysis of radionuclides providing comprehensive information on the possible source of actinides in the environment [11].

Several sample preparation methods have been applied for the separation of plutonium and americium from environmental samples, involving co-precipitation methods [12], anion ion-exchange [13,14] and extraction chromatographic separation [15,16]. Since sample preparation methods for radionuclide analysis are tedious, time and chemical consuming, and the sample collection is often difficult and expensive, it is favourable to analyze as many radionuclides as possible on a minimum sample amount. Sequential extraction procedure allows the determination of a number of actinides in the same sample aliquot [17]. Another advantage of the sequential sample preparation methods is that the sample can be characterised more comprehensively if as much anthropogenic radionuclides are determined as possible. The sample preparation method used in this work was developed for simultaneous analysis of radionuclides and has been reported in details elsewhere [18]. The method is a sequential sample preparation procedure using a co-precipitation step for pre-concentration and a separation step applying extraction chromatographic resins (TRU and UTEVA) for purification and separation of radionuclides. However, the method allows the simultaneous determination of thorium, neptunium, plutonium and americium from the same sample aliquot, this study focused only on the determination of americium and plutonium in environmental samples.

The aim of this study is to evaluate the application of the analytical procedure based on ICP-SFMS in comparison with alpha spectrometry for the determination of americium and plutonium and describe the possibility of sample characterisation by isotopic composition. Possible interferences in mass spectrometric analysis caused by molecular ions of mercury and lead isotopes e.g. $^{200}\text{Hg}^{40}\text{Ar}^+$, $^{204}\text{Pb}^{36}\text{Ar}^+$, $^{208}\text{Pb}^{16}\text{O}_2^+$ or uranium hydride formation ($^{238}\text{U}^1\text{H}^+$) [19] were eliminated

mainly in the co-precipitation/pre-concentration step, where Pu and Am were selectively separated from the sample matrix. Additionally, the molecular interferences caused by oxide and hydride formation in the plasma were efficiently reduced by using a desolvation system [20]. The current report presents the details of development of ICP-SFMS method as well as results for certified reference materials and environmental samples collected in Ukraine and Russia. The analytical figures of merit of ICP-SFMS and alpha spectrometry analysis are presented and the advantages and disadvantages of both methods are discussed. The characterisation and possible origin of samples by plutonium and americium isotopic composition are described.

2. Materials and methods

2.1. Standards and reagents

The ^{242}Pu (NIST 4334F, USA) and ^{243}Am (Amersham International, UK) isotopic standards were used to spike the samples. The standard solutions were diluted by weight to obtain stock solutions with a concentration of 200 pg g^{-1} . Multielement standard solution purchased from Merck (Darmstadt, Germany) was used for the optimization of the ICP-SFMS instrument. Natural uranium solution was used to correct for mass discrimination.

The UTEVA (100–150 μm particle size, active component: dipentyl-pentyl phosphonate) and TRU (100–150 μm particle size, active component: octylphenyl-*N,N*-di-isobutyl carbamoylphosphine oxide dissolved in tri-*n*-butyl phosphate) extraction chromatographic resins were supplied by Eichrom Technologies Inc. (Darien, Illinois, USA). For the analysis, 1.4 ml of the resin was placed in plastic Bio-Rad holders (diameter: 8 mm, length: 40 mm) and plugged with glass wool on the top of the resin to avoid mixing.

All reagents used were of analytical grade. Nitric and hydrochloric acids used in the final solution for ICP-MS analysis were Suprapur grade (Merck, Darmstadt, Germany). For dilution of reagents and samples de-ionised water was used (Option 4, Elga LabWater, USA). All sample preparation and measurement procedures were carried out under clean room conditions (class 100 000).

The analyzed certified reference materials were IAEA-384 (Fangataufa lagoon sediment) and IAEA-385 (Irish Sea sediment) supplied by the International Atomic Energy Agency. No additional drying or homogenization was carried out on standard reference materials.

2.2. Sample collection and sample preparation

The Chernobyl soil sample was collected within the 30 km exclusion zone. The sampling site of the Mayak soil is not exactly known, the sample was confiscated from illegal transport. After weighing the homogenized soil samples (0.5–3 g depending on the concentration level) into PFA microwave digestion vessels known amounts of ^{242}Pu and ^{243}Am were added to the samples. Following the addition of

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